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INFRARED, CORRELATION, AND FOURIER TRANSFORM SPECTROSCOPY

EDITED BY

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**INFRARED, CORRELATION,
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SPECTROSCOPY**

- Volume 1:* Computer Fundamentals for Chemists
- Volume 2:* Electrochemistry: Calculations, Simulation, and Instrumentation
- Volume 3:* Spectroscopy and Kinetics
- Volume 4:* Computer-Assisted Instruction in Chemistry (in two parts).
Part A: General Approach. Part B: Applications
- Volume 5:* Laboratory Systems and Spectroscopy
- Volume 6:* Computers in Polymer Sciences
- Volume 7:* Infrared, Correlation, and Fourier Transform Spectroscopy

INTRODUCTION TO THE SERIES

In the past decade, computer technology and design (both analog and digital) and the development of low cost linear and digital "integrated circuitry" have advanced at an almost unbelievable rate. Thus, computers and quantitative electronic circuitry are now readily available to chemists, physicists, and other scientific groups interested in instrument design. To quote a recent statement of a colleague, "the computer and integrated circuitry are revolutionizing measurement and instrumentation in science." In general, the chemist is just beginning to realize and understand the potential of computer applications to chemical research and quantitative measurement. The basic applications are in the areas of data acquisition and reduction, simulation, and instrumentation (on-line data processing and experimental control in and/or optimization in real time).

At present, a serious time lag exists between the development of electronic computer technology and the practice or application in the physical sciences. Thus, this series aims to bridge this communication gap by presenting comprehensive and instructive chapters on various aspects of the field written by outstanding researchers. By this means, the experience and expertise of these scientists are made available for study and discussion.

It is intended that these volumes will contain articles covering a wide variety of topics written for the nonspecialist but still retaining a scholarly level of treatment. As the series was conceived it was hoped that each volume (with the exception of Volume 1

which is an introductory discussion of basic principles and applications) would be devoted to one subject; for example, electrochemistry, spectroscopy, on-line analytical service systems. This format will be followed wherever possible. It soon became evident, however, that to delay publication of completed manuscripts while waiting to obtain a volume dealing with a single subject would be unfair to not only the authors but, more important, the intended audience. Thus, priority has been given to speed of publication lest the material become dated while awaiting publication. Therefore, some volumes will contain mixed topics.

The Editors

PREFACE

For years, while much of the spectroscopic instrumentation market was ignoring the inroads being made into the laboratory by minicomputers, and now by microprocessors, individual researchers were deeply involved in the mating of laboratory "workhorse" instruments and powerful laboratory computers. As Norman Jones states in Chap. 1 of this volume, his laboratory began the move to computer-aided infrared data handling in 1960. The major infrared instrument manufacturers did not introduce a computer-interfaced spectrophotometer to the commercial market until 1975, years after similar systems were in existence in several university and industrial laboratories around the country.

Chapters 1 and 2 of this volume focus on infrared spectroscopic data-handling possibilities (Chap. 1) and laboratory data acquisition (Chap. 2). Both of these authors have used the same commercial infrared spectrophotometer as their data source in their laboratories. In Chap. 1, N. Jones of the National Research Council of Canada describes fifty computer programs developed in his laboratory over a period of fifteen years, from simple transmittance-absorbance conversion routines to complicated band deconvolution programs. In Chap. 2, J. Mattson and C. A. Smith describe an on-line minicomputer data system for the Perkin-Elmer model 180 infrared spectrophotometer in sufficient detail that the reader needs little else to be able to duplicate their system. The data system described by Mattson and Smith in Chap. 2 would make an ideal complement to the data reduction programs described by Jones in Chap. 1.

In Chap. 3, R. Wiens and H. Zwick of Barringer Research Ltd. share the innovative notions of correlation spectroscopy applied to measurement of gaseous pollutants in the atmosphere. They describe the whole range of correlation spectroscopic techniques from the dual-chambered gas-filled detector developed by Luft in 1938 to a satellite-borne, Fourier transform correlation spectrometer developed by Barringer Research to locate sources and sinks of CO in the earth's atmosphere. Correlation Fourier transform spectroscopy borrows from many fields of modern spectroscopy to provide a singularly powerful remote sensing device for single gaseous species, for example, SO₂, NO, CO. Wiens and Zwick provide the reader with enough of the theory of correlation spectroscopy, and descriptions of the requisite hardware and electronics, that individuals with only a rudimentary background in analytical spectroscopy will be able to understand their chapter. Furthermore, there is sufficient detail in the chapter that some may be tempted to go out and build their own instrument.

In Chap. 4, C. Foskett of Digilab delves into the rationale behind choosing a laboratory minicomputer, comparing the needs of a dispersive infrared spectrophotometer with a Fourier transform infrared interferometer. Foskett explains the requirements for a laboratory computer in terms of the rate of information to be transferred and the information content of each datum. In describing the criteria to be employed by a potential minicomputer user, Foskett uses a Data General NOVA as his "model" system. His discussion thus nicely complements Mattson and Smith's chapter, where the same family of minicomputers is employed in conjunction with a dispersive infrared spectrophotometer.

Washington, D. C.

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Chapter 1

MODULAR COMPUTER PROGRAMS FOR INFRARED SPECTROPHOTOMETRY

R. Norman Jones

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I. INTRODUCTION

Our laboratory first used a computer to analyze infrared spectral data in 1960 when we developed a program to compute the second, third, and fourth truncated moments to quantify the shape and asymmetry of infrared absorption bands [1]. The spectrum was measured on a single-beam grating spectrometer and the chart was hand-digitized in terms of the wave number and the absorbance. The program was written in machine language for the IBM 1620 computer; a description was published in 1962 [2].

In 1961 we began to write programs in FORTRAN II, still working with data digitized from the recorder chart and punched on Hollerith cards. These programs were written in connection with the preparation of wave number calibration tables [3] and for the intensity

calibration of infrared spectrophotometers with high-speed rotating sectors [4]; IBM 650 and 1620 computers were used.

Our experience with direct digital data logging began in 1963 when we acquired a Perkin-Elmer Model 421 spectrophotometer with direct encoding on paper tape. The organization of the set of programs that forms the basis of this chapter began at that time. The data logging system, as it was operating in 1967, has been described [5,6]. Parts of that system are still in use for the measurement of attenuated total reflection spectra, but the main work of the laboratory is now channeled through a Perkin-Elmer Model 180 spectrophotometer with magnetic tape encoding. Once in storage the data can be accessed from a time shared terminal in the laboratory with an on-line plotter adjacent to the terminal.

During the past decade most of our work has involved computer processing of digitally recorded spectral data and a wide range of programs has been written. In our own operations most of the programs are incorporated as subroutines in automated systems for spectrophotometer calibration, data reduction, and spectral analysis, but concomitant with the development of this integrated system a modular set of independent programs has been prepared. Twenty-two of these modular programs were published in 1968-1969 [7-9] and an additional 28 more recently developed programs will soon be available [10-13]. They are listed by title in an appendix to this chapter and may be obtained from our laboratory (see note 1).

In this chapter the functions and general structure of the programs are outlined. They are all written in FORTRAN IV and are designed for card input and card and printed output. Each program executes a specific type of spectrophotometric calculation and collectively they will perform most of the basic calculations of absorption spectrophotometry. A defined set of abscissal and ordinate scales is used and there are programs for scale and unit conversion. The FORTRAN terminology and the input and output card formats are standardized to facilitate the interfacing of the programs; in most cases the numerical sections of the card output from one program can be used directly as input to others.

Our laboratory deals mainly with the infrared spectra of condensed phase systems, but the use of the programs in other fields of vibrational and electronic spectroscopy is facilitated by Program II which provides for interchange between wave number scales in reciprocal centimeters and wavelength scales in micrometers and angstroms with retention of equal interval abscissal digitization.

It must be emphasized at the outset that in writing these programs the main intent has been to convey the algorithms in a readable form, and no claim is made for high computational efficiency. It is a truism that as computer programs are edited to increase their efficiency as means to communicate between man and machine, they become decreasingly effective as means to communicate between mind and mind through direct human intelligence. It was not our purpose in preparing these programs to create a series of computationally efficient "black boxes." Rather we wished to convey to chemists and spectroscopists some of our experience in formulating the underlying algorithms in computer readable language. One would anticipate that each user will wish to adapt the programs to operate with optimal efficiency within the framework of the configuration of his own computer system. This applies particularly to the very simple card image input and output formats which are capable of considerable compression, especially if the user is prepared to forego the generalized interfacing potential and link them directly as subroutines. Storage requirements, of particular importance to those working with minicomputers, can be reduced by more efficient overlay of the arrays and more sophisticated nesting of the do-loops.

II. ORGANIZATION OF THE RAW SPECTRAL DATA

The standard formats for the abscissal and ordinate scales used for card output in these programs are summarized in Table 1. The abscissal units of wavelength and wave number are the conventional ones in molecular spectroscopy except for $\text{cm}^{-1} \times 10$ (see note 2). This is a convenient unit for the manipulation of infrared wave number data with five-figure precision in fixed point arithmetic.

TABLE 1
Standardized Card Input and Output Formats

	Transmittance	Transmittance × 1000	Absorbance	Molar absorption coefficient	Absorption index
Cm^{-1}	6(F6.1,F6.3,1X)	7(F6.1,I4,1X)	6(F6.1,F6.3,1X)	5(F6.1,F7.2,1X)	5(F6.1,F7.4,1X)
$\text{Cm}^{-1} \times 10$	6(I5,F6.3,1X)	8(I5,I4,1X)	6(I5,F6.3,1X)	6(I5,F7.2,1X)	6(I5,F7.4,1X)
Micrometers	6(2F6.3,1X)	7(F6.3,I4,1X)	6(2F6.3,1X)	5(F6.3,F7.2,1X)	--
Angstroms	5(F8.1,F6.3,1X)	6(F8.1,I4,1X)	5(F8.1,F6.3,1X)	5(F8.1,F7.2,1X)	--